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Effect of Groundwater Age and Recharge Source on Nitrate Concentrations in Domestic Wells in the San Joaquin Valley

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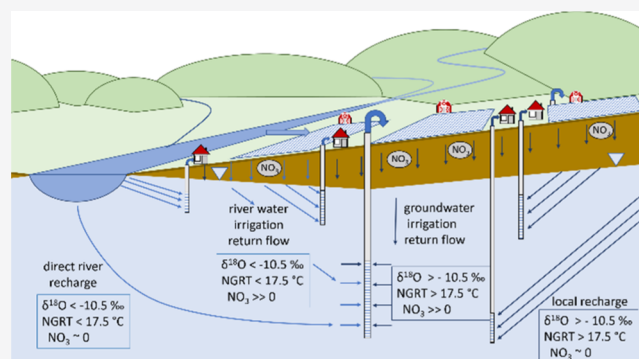


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ABSTRACT: Nitrate is one of the most abundant contaminants in groundwater globally, in the United States, and in California (CA). We studied well construction information, water chemistry, stable isotopes, and noble gases to understand how groundwater travel time and recharge source and mechanism control nitrate concentrations in domestic wells in the San Joaquin Valley (SJV), CA, a large semiarid, irrigated agricultural region. Using non-parametric statistics, we find a decreasing trend in nitrates with groundwater travel time and well depth. Samples collected from wells that are closer to rivers and that show indications of river water recharge, either low recharge temperature or low $\delta^{18}\text{O}$ signature, have lower concentrations of nitrates than samples with isotopic signatures indicating mixed source or local precipitation recharge. The curbing effect of river water recharge on nitrate concentrations in domestic wells is similar for direct river recharge and water applied as irrigation. This suggests that irrigation with river water also has a diluting effect that reduces the concentration of nitrate found in groundwater. This conclusion supports the idea that flood-managed aquifer recharge may be considered for remediation of groundwater nitrate when designing replenishment of aquifers.



INTRODUCTION

Two-thirds of the San Joaquin Valley (SJV) is used for agricultural production with an annual gross value of more than \$25 billion from more than 250 different crops.^{1–3} The SJV is also home to three-quarters of California's dairy herd. In California, as in other areas in the world of intensive agriculture, the wide-spread, long-term application of fertilizers and manure is identified as the main cause of nitrate (NO_3) contamination of groundwater.^{4,5} The fraction of applied N that leaches into groundwater as nitrates ranges from ~5 to 50%, depending on local conditions.^{6–13} In the SJV, as much as 88 kg N/ha/year may leach into groundwater in areas where fertilizers are applied.^{1,14} Increasing trends in nitrate levels in SJV groundwater during the 1950s and 1960s and from the 1970s to 1980s correlated with an increase in fertilizer and manure use and an increase in the dairy herd size in confined animal feeding operations.^{1,15} Among the nine hydrogeologic provinces in California, the SJV was found to have the largest area affected by high groundwater nitrate.^{16,17}

Nitrate is one of the most abundant contaminants in groundwater globally, in the United States, and in California.^{18–21} The United States Environmental Protection Agency (USEPA) regulates $\text{NO}_3\text{-N}$ (the quantity of nitrogen present in nitrate form) at a maximum contamination level (MCL) of 10 mg/L because it can cause methemoglobinemia in infants and may be associated with some types of cancer.^{18,19,22,23} In the eastern fan subregion of the California

Central Valley (CV), the nitrate concentration increased 4-fold in the shallow aquifer and 2-fold in the deep aquifer from the 1950s to the 2000s.^{16,24} As opposed to deeper public supply wells, shallower domestic wells are not regulated in California and not subject to regular water quality monitoring. As a result, domestic wells are underrepresented in groundwater quality monitoring data. The approximately 350,000 people living in 450 disadvantaged unincorporated communities throughout the SJV are at the greatest risk of exposure to unsafe drinking water.²⁵ According to recent estimates, it is likely that about 100,000 people who rely either on domestic wells or on community water systems that are out of compliance drink unsafe water in the SJV alone.²⁵ The great majority of these residents who lack access to clean, safe, and affordable drinking water are people of color who also face the cumulative impacts from environmental contamination brought on by proximity to air pollution, pesticides, toxic facilities, and waste disposal.²⁵

Important factors influencing N concentrations in groundwater include application rates of N, water input, soil texture,

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vadose zone thickness, evapotranspiration, reduced geochemical conditions, and well construction characteristics such as well depth.^{1,6,11,24,26–32} In addition, numerical models show that source area distributions, travel times, and geochemical indicators of denitrification rate are also relevant to understand groundwater N contamination.^{6,33–40} These studies on nitrate concentration trends in groundwater point at three broad controlling factors: (1) historical inputs and outputs (water recharge rate, evapotranspiration and N loading rate), (2) groundwater travel time (soil/sediment texture, depth of vadose zone, well depth, and geological characteristics), and (3) geochemical reactions along the groundwater flow path (most importantly denitrification).

In the SJV, the proportion of river water recharge nearly doubled since the 1950s because of increased irrigation with river water, increased stream depletion, and direct river recharge due to losing conditions induced by groundwater pumping.⁴¹ Proximity to rivers ranked in the top 10 predictors of nitrate concentration—right after proxies of reduced geochemical conditions, historical inputs and outputs, and groundwater travel time—in a hybrid machine learning model.¹⁶ Predicted nitrate concentrations less than background level (2 mg/L) correlated with short distance to rivers.¹⁶ Wells nearer to rivers are likely to have lower nitrate concentrations due to low nitrate concentration in infiltrating river water.^{16,42}

In this context, the idea of flooding agricultural land during fallow or dormant periods using winter high magnitude surface water flows to recharge depleted aquifers is gaining traction in California. Studies have found that 3.6 million acres of agricultural land statewide has excellent or good potential for flood-managed aquifer recharge (flood-MAR), and in an average year with high-magnitude flows (HMF), approximately 3.2 km³ of HMF that could be used for flood-MAR is exported from the entire Central Valley.^{43,44} Mobilization of arsenic and other trace metal contaminants during flood-MAR poses a challenge to maintaining local groundwater quality while recharging the aquifer.⁴⁵ Another risk related to flood-MAR is that legacy nitrate can be flushed from the vadose zone and increase nitrate concentrations in groundwater. In fact, nitrate is found to be flushed down into the deeper vadose zone in field and soil column flooding experiments.⁴⁶ Additional nitrate also forms in the upper root zone due to organic nitrogen mineralization and nitrification facilitated by the added water.⁴⁶ Nevertheless, recent studies suggest that denitrification and long-term flushing with clean river recharge water can lower nitrate concentrations in the aquifer during flood-MAR.^{47,48}

The objective of our study is to evaluate the effect of groundwater recharge with river water (negligible NO₃-N relative to the MCL), well depth, and groundwater travel times on nitrate concentrations in domestic drinking water wells in the San Joaquin Valley. We use the $\delta^{18}\text{O}$ water signature, the noble gas recharge temperature (NGRT), the proximity to rivers, and the surface water sources of the irrigation districts providing irrigation water in the vicinity of each domestic well location to test the hypothesis that river water recharge (either direct recharge or as irrigation return flow) results in lower nitrate concentrations than local precipitation recharge or groundwater irrigation. We use several sample depth indicators and tritium-helium (³H/³He) groundwater ages to test the hypothesis that nitrate concentrations are higher in younger and shallower groundwater pumped by domestic wells. We focus our statistical analyses on oxic and modern groundwater

samples to limit the influence of denitrification and of mixing with old groundwater on groundwater nitrate concentrations.

MATERIALS AND METHODS

Study Area. The San Joaquin Valley (SJV) encompasses the southern two-thirds of the Central Valley of California. It is a large alluvial basin surrounded to the north by the Sacramento–San Joaquin Delta, to the south by the Tehachapi Mountains, to the east by the Sierra Nevada Mountains, and to the west by the Coast Ranges. It is approximately 400 km long and 95 km wide at its widest location. Perennial, unpolluted streams emerge onto large alluvial fans directly from their pristine headwaters in the Sierra Nevada, along the eastside of the study area. Irrigation diversions are mostly from storage reservoirs located at the bottom of the Sierra Nevada, just above the SJV basin. Tertiary to Holocene age, unconsolidated continental, lacustrine, and marsh deposits comprise the upper 500 to 1000 m of the SJV basin, where fresh groundwater is found. The SJV is divided into two sections: the San Joaquin Groundwater Basin which is drained by the San Joaquin River and its tributaries in the north, and the Tulare Groundwater Basin which is drained by the Kings, Kaweah, Kern, and Tule Rivers into the semiterminal Tulare Lake in the south.² The northern section of the SJV has shallower groundwater levels compared to the southern section. Throughout the SJV, groundwater levels are deeper at the alluvial margins against the surrounding mountains and most shallow along the valley trough.

Data Sources. We combine data collected from domestic wells from three different datasets, representative of two-thirds of the San Joaquin and Tulare Groundwater Basins, focusing on areas east of the valley trough and north of Kern County. The first is a set that consists of 200 samples from private domestic wells, collected between 2010 and 2011: 100 in the Stanislaus and Merced Counties, and 100 in the Tulare and Kings Counties.¹ The collection protocol used with these samples is reported in Lockhart et al.¹ They were analyzed for nitrate, ion chemistry, heavy metals, stable isotopes of water, nitrate, and carbon, and ³H/³He groundwater age.⁴⁹ The second dataset encompasses 95 domestic wells sampled in the Tulare and Kings subbasins between 2014 and 2015, while the third dataset includes 77 domestic wells sampled in the Madera, Chowchilla, and Kings subbasins between 2013 and 2014. These latter 172 wells were sampled for the Tulare Shallow Aquifer Study Unit and the Madera/Chowchilla-Kings Shallow Aquifer Study Unit, respectively, of the California State Water Resources Control Board Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project's assessment of the quality of groundwater resources used for domestic drinking water supply.^{50,51} Groundwater samples were analyzed for field water-quality parameters, volatile organic compounds, pesticides and pesticide degradates, nutrients, major ions and trace elements, gross alpha and gross beta particle activities, noble gases, tritium (³H), carbon-14 in dissolved inorganic carbon, stable isotopic ratios of hydrogen and oxygen of water and nitrogen and oxygen of dissolved nitrate, and microbial indicators.^{50,51}

River Water Signature. In our analysis, we consider two major sources of water to the SJV groundwater system each of which has a distinct stable isotope signature: local precipitation recharge and river water recharge (including contributions from the State Water Project). Hydrologically, the irrigation return flow of pumped groundwater also contributes

significantly to recharge. However, recycled recharge of pumped groundwater is isotopically indistinguishable from the original pumped groundwater and as such reflects the original source of recharge, be it local precipitation recharge, river water recharge, or a mixture of both.

To understand the impact of river water recharge, we use their distinct stable isotope signatures (specifically the oxygen isotopic ratio) to track river water recharge and local precipitation recharge through the SJV groundwater system.⁴¹ In California, the physiographic gradient from the Pacific Ocean maritime climate (relatively warm and constant temperatures) to the alpine climate of the Sierra Nevada (at 3,000 m to over 4,000 m elevation, cold and widely fluctuating temperatures) results in a large range of stable isotope ratios in precipitation.⁴¹ The “continental effect”, whereby water vapor becomes isotopically lighter as it moves inland because the heavier isotope rains out, further controls the stable isotope pattern in precipitation in California.⁵² The oxygen isotopic ratio in water is defined as $\delta^{18}\text{O}$

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000\text{‰} \quad (1)$$

where R_{sample} and R_{standard} are the $^{18}\text{O}/^{16}\text{O}$ ratios for the sample and standard, respectively. All $\delta^{18}\text{O}$ data are reported in per mil (‰) relative to Vienna standard mean ocean water. The stable isotopic signature of river water is highly depleted in heavier isotopes (resulting in more negative $\delta^{18}\text{O}$ values) as a result of streamflow dominated by high elevation snowmelt in the source areas of the rivers.⁴¹ The $\delta^{18}\text{O}$ source signature of local precipitation recharge and of the main rivers draining the study area were taken from literature sources.⁴¹ Local precipitation recharge has a mean $\delta^{18}\text{O}$ signature of -8.2‰ (± 0.2) based on samples from shallow low-elevation wells in the foothills and an extrapolation of the elevation $\delta^{18}\text{O}$ lapse to the valley floor elevation.⁴¹ The flow weighted average river signature (-12.7‰) was calculated as the mean $\delta^{18}\text{O}$ of all rivers flowing into the SJV weighted by their annual flow.⁴¹ The weighted average $\delta^{18}\text{O}$ signature of these two recharge sources, reflecting the average input of all recharge sources in the SJV, is -10.9‰ .

Wells in these three datasets were classified by their respective overlying irrigation district using the Water Management Planning Tool (<https://gis.water.ca.gov/app/boundaries/>), available through the California Department of Water Resources (DWR). When available, the agricultural management plans filed by each district were used to determine the sources of river water provided for irrigation purposes. The rest of the districts were contacted directly by phone to request information on river sources used to allocate water to their customers (Table S1). Each well was assigned a surface water irrigation $\delta^{18}\text{O}$ signature following two main assumptions: (1) only the main rivers that drain the SJV are relevant as they are the dominant surface sources of irrigation water and (2) waters from multiple rivers listed by an overlying district each had a statistically equal likelihood to impact the domestic well sampled.

The lowest $\delta^{18}\text{O}$ values ($\delta^{18}\text{O} < -12.5\text{‰}$) for irrigation water are concentrated in the area between the San Joaquin River and Kaweah River, where irrigation districts divert water from rivers with the region's highest elevation ($>4,000$ m) headwaters: the Kings, San Joaquin, Kaweah, and St. John's River (Figure S1). The highest $\delta^{18}\text{O}$ values in river water are found in the Tule River (<2500 m), which has a $\delta^{18}\text{O}$ signature of -10‰ .⁴¹ Each well's $\delta^{18}\text{O}$ signature ($\delta^{18}\text{O}_{\text{GW}}$) was

compared against the overlying surface water irrigation $\delta^{18}\text{O}$ signature ($\delta^{18}\text{O}_{\text{RWR}}$) and the local precipitation recharge signature ($\delta^{18}\text{O}_{\text{LPR}}$) to calculate the fraction of river water recharged near that well (f_{RWR}), assuming linear mixing between the two endmembers (river water recharge and local precipitation recharge)⁴¹

$$f_{\text{RWR}} = (\delta^{18}\text{O}_{\text{GW}} - \delta^{18}\text{O}_{\text{LPR}})/(\delta^{18}\text{O}_{\text{RWR}} - \delta^{18}\text{O}_{\text{LPR}}) \quad (2)$$

The presence of river water signature in the samples can be due to the river water applied as irrigation in the fields nearby the wells or due to water lost by seepage into the ground from a nearby losing river.⁵³ Open water evaporation of irrigation can cause fractionation of hydrogen and oxygen isotopes of water resulting in a shift away from the local water line. The effect of evaporative fractionation would be a shift in $\delta^{18}\text{O}$ toward the local precipitation recharge endmember and a smaller estimated proportion of river water in the sampled groundwater mixture. In our analyses, we did not consider the isotopic shift due to evaporative fractionation in the calculation of the fraction of river water recharge because all samples plot closely to the local water line established on a larger data set of SJV groundwater, indicating that there was no strong evidence for evaporative enrichment (Figure S2).⁴¹

To gain more insights into the relationship between $\text{NO}_3\text{-N}$ in a domestic well and its river water signature, the well's proximity to rivers was examined. The flowlines of rivers of stream order 4, which include all main SJV rivers, were obtained from the National Hydrography Dataset (<https://www.usgs.gov/core-science-systems/ngp/national-hydrography>). The R library “rgeos” was used to obtain the distance of the wells to the closest river. In the northern SJV, the Stanislaus, Tuolumne, and Merced Rivers are losing in their upper and middle reaches and become gaining streams in their lower reaches about two-thirds of the way toward the valley trough.^{54–56} On the other hand, rivers coming from the southern part of the Sierra Nevada and the Coast Ranges into the Tulare Basin generally are losing streams along their entire length.^{54–56} Groundwater levels,⁵⁷ when compared to stream elevations, confirm this general trend. Bear Creek was added to the group of northern rivers that become gaining in their lower reaches. For the great majority of domestic wells (252 out of 264), the river stretch that is closest to the well is a losing stretch, indicating that direct river recharge is an important factor to take into consideration.

Redox. A key process that potentially determines the fate of NO_3 in groundwater is denitrification.¹⁸ To evaluate the impact of denitrification on the concentration of NO_3 in domestic wells, redox conditions of the well samples were assessed following the classification system of McMahon and Chappelle, 2008.⁵⁸ Under this classification system, threshold values of redox indicators are 0.5 mg/L for O_2 , 0.5 mg/L for $\text{NO}_3\text{-N}$, 0.05 mg/L for Mn, 0.1 mg/L for Fe, and 0.5 mg/L for SO_4 . The redox classification scheme includes redox categories: oxic, mixed, and anoxic.¹⁸ All samples with O_2 above the threshold and without other indicators (Mn, Fe) above their thresholds were categorized as “oxic”.¹⁸ Samples with a mixed redox category contain O_2 or $\text{NO}_3\text{-N}$ and another indicator (Mn or Fe) above thresholds.¹⁸ Samples with an anoxic redox category contain O_2 below the threshold and one or more other indicators (Mn, Fe) above thresholds.¹⁸ The mixed and anoxic categories are condensed into a “not oxic” category in this study.

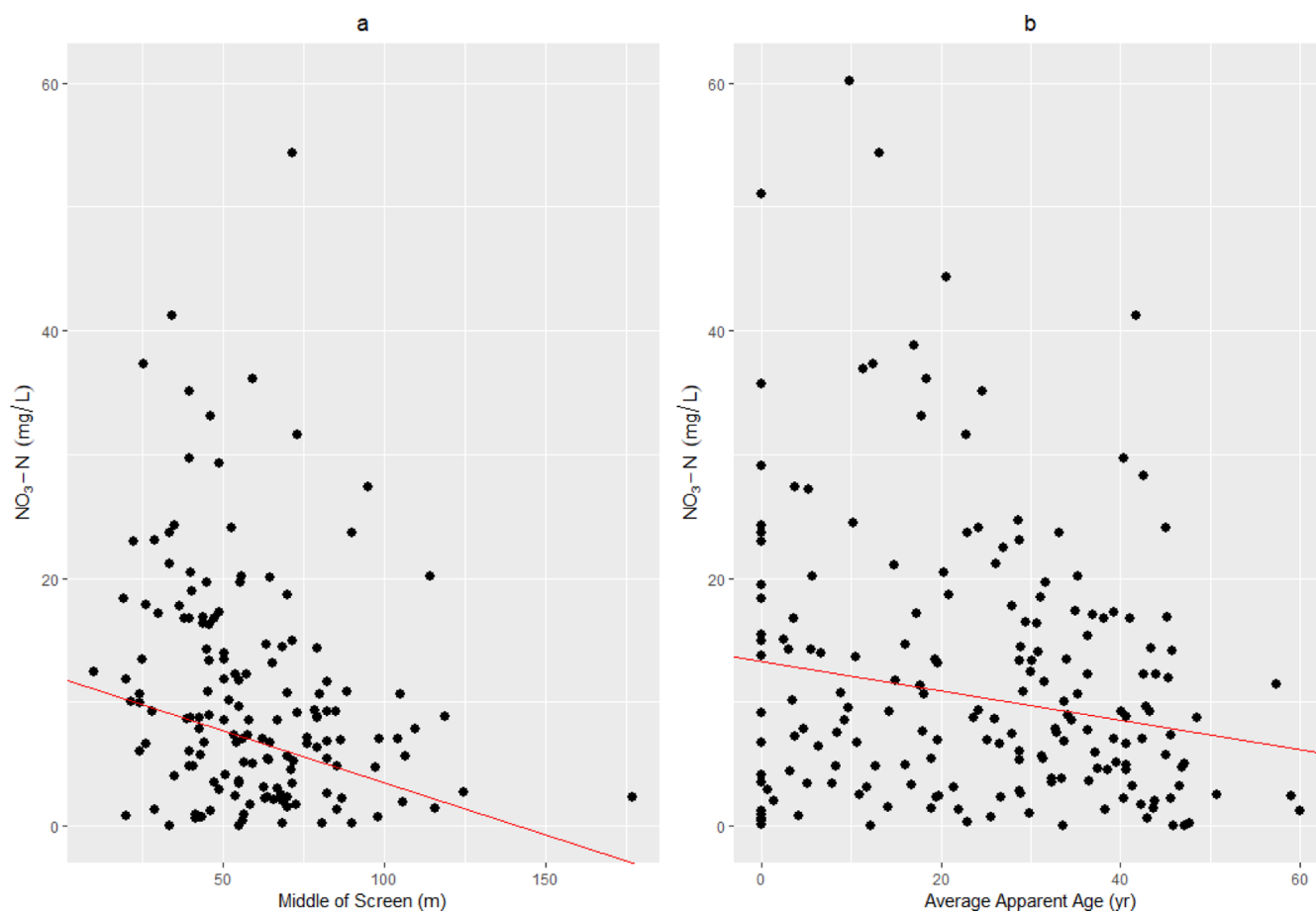


Figure 1. NO₃-N versus sample depth (middle of screen, 152 wells) (a) and average apparent age (185 wells) (b). The trend lines (red) are obtained using KTSS regression.

Noble Gas-Derived Parameters. Noble gas-derived parameters [recharge temperature, excess air, terrigenic helium-4 (⁴He_{ter}), terrigenic helium isotope ratio (R_{ter}), and tritiogenic helium-3 (³He_{trit})] were calculated using the unfractionated excess air model.^{59,60} This model was used in order to avoid bias in derived parameters resulting from the choice of the excess air model.^{59,61,62} The NGRT and excess air are calculated from Xe and Ne by solving a second-order polynomial that approximates the Ne and Xe concentrations for various temperatures and excess air amounts. The estimated NGRT and excess air are then tested against the Ar and Kr concentrations, and the χ^2 probability of the fit is calculated. If the probability is less than 1%, a bad fit for NGRT and excess air is reported. For samples with a detectable component of “modern” recharge (containing more than 1 pCi/L ³H), we calculated apparent ³H/³He groundwater ages as $\ln(^3\text{He}_{trit}/^3\text{H} + 1)/0.05626$ following Visser et al.⁵⁹ The apparent age reflects the average travel time since crossing the water table for the fraction of modern groundwater (recharged since 1953) in pumped, mixed-age groundwater samples.^{18,31,62–64} ³H/³He ages with a propagated analytical uncertainty of more than 10 years were discarded from the analysis.

Statistical Methods. All relevant dependent variables (NO₃-N, $\delta^{18}\text{O}$, NGRT, f_{RWR}) are found to have non-normal distributions. Thus, nonparametric statistical tests are applied. The Kendall–Theil–Sen–Siegel (KTSS) nonparametric linear regression is used here to determine significant trends.^{65–67}

The method yields a slope and intercept for the fit line and a *p*-value for the slope. To determine whether the two groups of sample results differ significantly, the nonparametric Wilcoxon rank-sum test is used.^{68,69} When comparing more than two groups, the nonparametric Kruskal–Wallis test is employed instead.⁶⁹

RESULTS AND DISCUSSION

The levels of nitrate concentration found in these domestic wells document unprecedented but not unexpected,^{1,5,16,42} dramatically widespread contamination: of the 354 wells in the dataset with NO₃-N data, 268 (75.7%) are above the background level of 2 mg/L and 135 (38.1%) are above the USEPA’s MCL of 10 mg/L. We focus our analysis on 264 samples that contain detectable ³H and therefore a component of recharge that occurred since the 1950s (³H > 1 pCi/L, referred to as “modern” groundwater, potentially affected by modern-day agriculture)^{59,70} and oxic (likely not affected by denitrification). Of this “modern and oxic” subset, 228 wells (86.4%) have a NO₃-N concentration above the background level and 116 wells (43.9%) above the MCL.

Sample Depth and Average Apparent Age. In the shallow aquifer, the superposition of regional, horizontal groundwater flow with the downward gradient induced by water table recharge and deeper groundwater production yields a groundwater flow field that is vertically inclined relative to the slope of the water table.⁷¹ Well samples are a mix of water from across the vertical extent of the well screen: younger

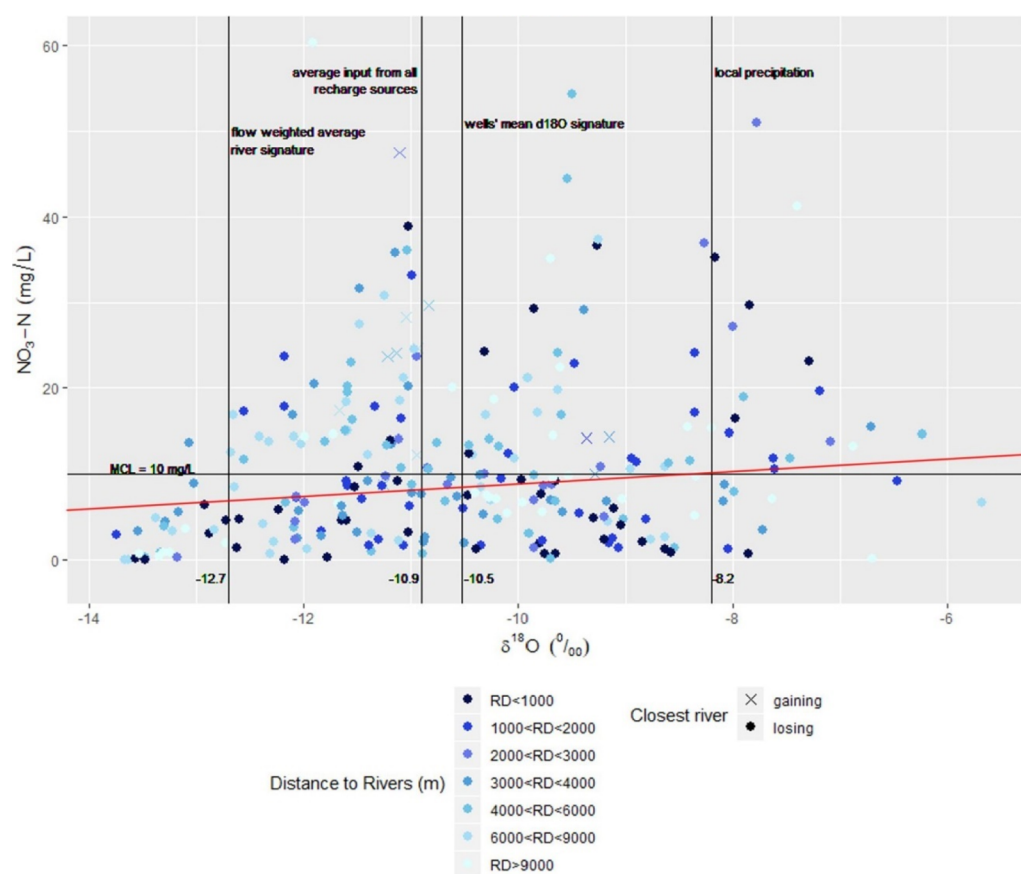


Figure 2. $\text{NO}_3\text{-N}$ versus $\delta^{18}\text{O}$. $\text{NO}_3\text{-N}$ correlates significantly with $\delta^{18}\text{O}$, indicating that a larger proportion of river water recharge leads to lower nitrate concentrations in domestic wells in the San Joaquin Valley. None of the wells with extremely high $\text{NO}_3\text{-N}$ concentrations is in the river water signature group. The trend line (red) is obtained using KTSS regression.

water enters the top of the screen and older water from further away in the capture zone enters the bottom of the screen. Even at localized screen intervals (<1 m), dispersion and heterogeneity of hydraulic conductivity produce enough age mixing for water ages within individual water samples to vary by an order of magnitude.^{35,40} Nonetheless, shallow wells with shorter groundwater travel distances and therefore young waters are expected to have a higher concentration of $\text{NO}_3\text{-N}$ than deeper wells that pump older water or a larger fraction of groundwater that recharged prior to historic increases in $\text{NO}_3\text{-N}$ losses from agriculture.^{5,40,72–74} Three proxies of well depth were available in the datasets: the depth of the borehole (172 wells) and the depths to the top and bottom of the well screen (152 wells). We used the midpoint between the top and the bottom of the screen interval as a fourth proxy of sample depth (152 samples). Publicly accessible water level data⁵⁷ were used to estimate the likely range of water table depth at each well location (237/264). From that, the location of the midpoint between the water table depth and the bottom of the borehole (155/264) was determined and used as a fifth proxy of sample depth. All five proxies are expressed as depth below land surface.

All five proxies of sample depth as well as the water table depth are negatively correlated with $\text{NO}_3\text{-N}$ concentration (Figure S3). While the five proxies represent the combined vadose zone and groundwater travel path of the water sampled, water table depth specifically indicates the effects of vadose zone travel time on $\text{NO}_3\text{-N}$. The depth to the center of the screen, available for 152 samples, is used as a proxy for further

analysis. Depth to the middle of screen varied from about 20 m to about 125 m. Using this proxy, $\text{NO}_3\text{-N}$ is found to decrease with depth at a rate of 0.084 mg/L per meter ($p < 0.001$) (Figure 1a).

Out of the 264 “modern and oxic” wells, we were able to calculate an apparent $^3\text{H}/^3\text{He}$ age for 185 samples with a propagated analytical uncertainty of less than 10 years. Average apparent age (“age”) varied widely among wells (0–60 years) but showed a significant correlation with $\text{NO}_3\text{-N}$, with $\text{NO}_3\text{-N}$ decreasing at 0.12 mg/L per year of age ($p < 0.001$) (Figure 1b). The “modern and oxic” trends in $\text{NO}_3\text{-N}$ with sample depth and age are most pronounced for the highest quartiles of the $\text{NO}_3\text{-N}$ concentration (Figure S4). As would be expected conceptually, higher $\text{NO}_3\text{-N}$ is more likely found in younger groundwater at shallower screen depths. In contrast, low concentrations are observed across all well depths and ages as some recharge continues to be low in nitrate.^{49,74} Despite improvements in agricultural practices,⁵ we expect nitrate concentrations in many domestic wells to increase in the future, when younger, shallower water with high $\text{NO}_3\text{-N}$ reaches deeper wells that currently produce mostly older water. Prior studies have found similar correlations.^{5,35,40,75} Even in “not oxic” wells, seven of the nine shallow-most samples, but only three of the nine intermediate and one of the eight deepest samples show $\text{NO}_3\text{-N} > 2$ mg/L (Figure S5). In “not oxic” samples, denitrification might contribute as a factor separate from age alone.

Recharge Source and Mechanism. The correlation between $\text{NO}_3\text{-N}$ and $\delta^{18}\text{O}$ for the “modern and oxic”

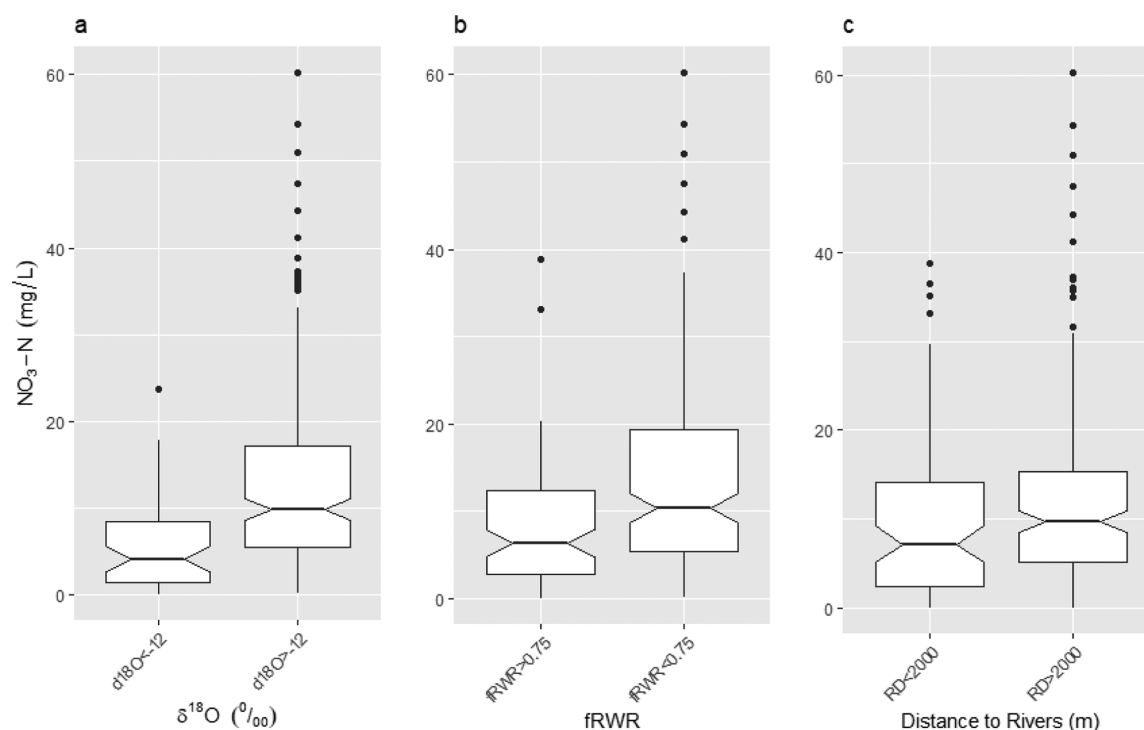


Figure 3. Boxplots showing the difference in $\text{NO}_3\text{-N}$ depending on $\delta^{18}\text{O}$ (a), fraction of river water recharged (f_{RWR}) (b), and distance to rivers (c). The notches indicate the 95% confidence interval of the median. The box shows the interquartile range.

domestic wells is significant, with an increasing trend of 0.72 mg/L per 1‰ increase in $\delta^{18}\text{O}$ ($p < 0.001$) (Figure 2). The distribution of $\text{NO}_3\text{-N}$ by $\delta^{18}\text{O}$ is displayed in Figure 2 with the flow weighted average river signature, the average input signature from all recharge sources, the local precipitation recharge signature of the SJV,⁴¹ the mean signature of the “modern and oxic” domestic wells in the dataset, and the $\text{NO}_3\text{-N}$ MCL.

The surface water irrigation signature averaged for all “modern and oxic” domestic well locations is $\delta^{18}\text{O} = -12.3\text{‰}$. In this analysis, we used $\delta^{18}\text{O} = -12\text{‰}$ as the threshold below which wells were identified as “river water” recharge. A second threshold to distinguish the recharge source of pumped groundwater is set at the average (-10.5‰) of the flow weighted average of river water recharge (-12.7‰) and local precipitation recharge (-8.2‰) endmembers. This value coincided with the mean d18O signature of all sampled wells, which is consistent with prior results that river water constitutes nearly 50% of modern groundwater in the San Joaquin Valley.⁴¹ Samples with a $\delta^{18}\text{O}$ value below -10.5‰ were considered to produce “predominantly river water”. The wells with a “river water” signature ($\delta^{18}\text{O} < -12\text{‰}$) have a lower concentration of $\text{NO}_3\text{-N}$ than other wells (Wilcoxon rank-sum test with continuity correction, $p < 0.001$) (Figure 3a). In comparison, the group of wells with a fraction of river water recharge (f_{RWR} , Eq. 2) of more than 75% also have a lower median $\text{NO}_3\text{-N}$ value than the group with $f_{\text{RWR}} < 75\%$ (Wilcoxon rank-sum test with continuity correction, $p < 0.001$) (Figure 3b). In contrast, the difference in median values is not significant between groups with more or less than 50% river water. Also, the wells that are further than 2 km from rivers were found to have higher $\text{NO}_3\text{-N}$ concentration than the ones that are closer than 2 km (Wilcoxon rank-sum test with continuity correction, $p < 0.05$) (Figure 3c). These findings

support the hypothesis that proximity to rivers is an important predictor of nitrate concentrations in groundwater.^{16,42}

Of the 264 “modern and oxic” domestic wells, 218 had sufficient noble gas data required to calculate a recharge temperature. The correlation between NGRT and $\delta^{18}\text{O}$ for the “modern and oxic” domestic wells is significant, with an increase of 0.43 °C per 1‰ increase in $\delta^{18}\text{O}$ ($p < 0.001$) (Figure 4) similar to a prior study of public-supply wells in the SJV.⁴¹ The mean recharge temperature of river recharge to SJV groundwater is 14.7 ± 3.0 °C,⁴¹ which is 3.9 °C cooler than the mean recharge temperature of all wells in this study (18.6 °C). A recharge temperature of 17.5 °C was set as an upper boundary for the range of temperatures indicative of “river water” recharge.

The wells with a recharge temperature indicative of “river water” recharge show a lower $\delta^{18}\text{O}$ than the wells with a NGRT > 17.5 °C (Wilcoxon rank-sum test with continuity correction, $p < 0.01$) (Figure 5a). The group of wells with NGRT < 17.5 °C also has lower concentrations of $\text{NO}_3\text{-N}$ than the group with NGRT > 17.5 °C (Wilcoxon rank-sum test with continuity correction, $p < 0.001$) (Figure 5b). Wells that display either one or both of the indicators of “river water” recharge (NGRT < 17.5 °C or $\delta^{18}\text{O} < -12\text{‰}$) have lower concentrations of $\text{NO}_3\text{-N}$ compared to the remainder of wells (NGRT > 17.5 °C and $\delta^{18}\text{O} > -12\text{‰}$) (Wilcoxon rank-sum test with continuity correction, $p < 0.001$) (Figure 5c). These findings further support the hypothesis that samples from domestic wells that show indications of “river water” recharge, either through NGRT or $\delta^{18}\text{O}$, have lower concentrations of $\text{NO}_3\text{-N}$ compared to samples that show mixed source or local precipitation recharge. These results confirm studies elsewhere that demonstrated that infiltration of river water into aquifers has a sizable dilution effect on $\text{NO}_3\text{-N}$.^{42,47,48}

The relationship between $\delta^{18}\text{O}$ (as an indicator of river water recharge) and distance to the nearest river is more

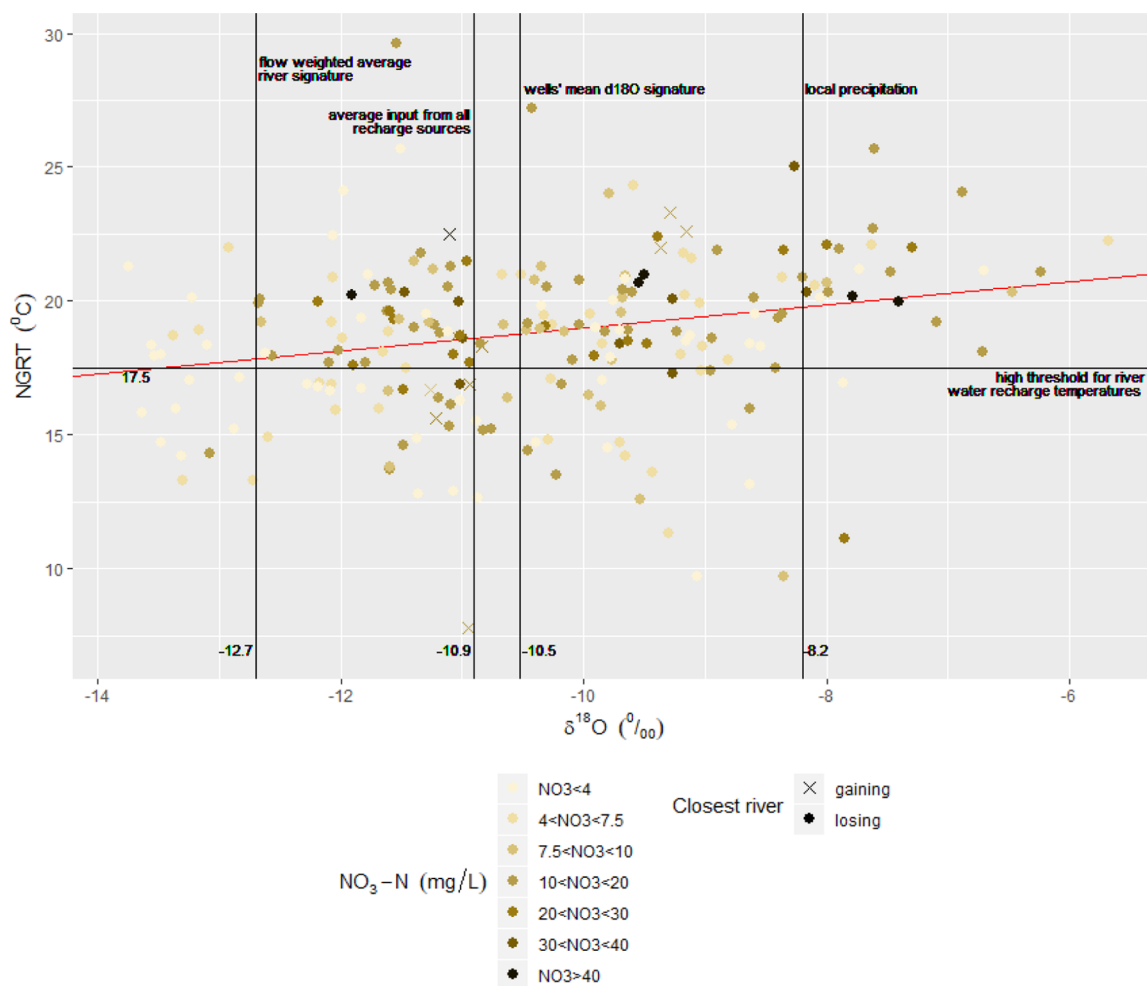


Figure 4. NGRT versus $\delta^{18}\text{O}$. The majority of wells below 17.5 °C and in the river signature group have $\text{NO}_3\text{-N}$ below MCL. The trend line (red) is obtained using KTSS regression.

complex: the mean $\delta^{18}\text{O}$ is lower, possibly indicating a larger fraction of river water, for wells that are 2 km or further from rivers (Wilcoxon rank-sum test with continuity correction, $p < 0.05$) (Figure S6a). Additionally, NGRT is not significantly different for within or outside the 2 km threshold (Figure S6b). In contrast, within and outside 1 km distance as a threshold, there is no significant difference in $\delta^{18}\text{O}$, but NGRT is significantly lower, as expected, in closer proximity to the river (Wilcoxon rank-sum test with continuity correction, $p < 0.05$) (Figure S6c). While we expected to find lower $\delta^{18}\text{O}$ signatures closer to the river, it appears that river water irrigation plays an important role in distributing river water across the landscape. The results suggest that the influence of direct river water recharge (as opposed to river water irrigation) on the NGRT of groundwater is limited to a short distance from the river, consistent with the strong regional downward gradient within the aquifer system. Our finding that $\delta^{18}\text{O}$ is not sensitive to river proximity further indicates that recharge after diversion and irrigation does not significantly change the $\delta^{18}\text{O}$ signature in the SJV when compared to direct recharge of river water. In contrast, diverted surface water in the Sierra Nevada foothills north of the SJV was found to recharge groundwater with a significant shift in $\delta^{18}\text{O}$ due to evaporative fractionation.⁷⁶

To study the effect of the recharge mechanism (direct river recharge or irrigation with river water), we examined the relationship between the distance to the river and nitrate

concentrations in the subset of wells with a predominance of river water signature ($\delta^{18}\text{O} < -10.5\text{‰}$) and a river water recharge temperature (NGRT < 17.5 °C). We assume that wells closer to rivers are more likely to be affected by direct river recharge, while those further away are affected primarily by surface water irrigation. We find no significant difference in $\text{NO}_3\text{-N}$ concentration with respect to river proximity with a threshold distance of either 1 or 2 km (Figure S7). This result suggests that the curbing impact of river water recharge on $\text{NO}_3\text{-N}$ concentration in domestic wells is effective for both direct recharge and irrigation water recharge.

While it is clear how direct clean river water recharge from losing streams acts to decrease $\text{NO}_3\text{-N}$ concentration by diluting or displacing contaminated groundwater, more research is needed to determine why irrigation recharge with river water leads to lower $\text{NO}_3\text{-N}$ concentrations. In past work, we have shown that groundwater irrigation fluxes are lower (more efficient) than river water irrigation fluxes⁷⁷ which leads to less dilution of vadose zone nitrate. Furthermore, higher nitrate concentrations in groundwater (when compared to river water) are not accounted for in nitrogen management decisions^{5,78} leading to lower nitrogen use efficiencies and higher $\text{NO}_3\text{-N}$ leaching under groundwater-irrigated crops. Some of the variability observed in the relationship between age, depth, $\delta^{18}\text{O}$, NGRT, and $\text{NO}_3\text{-N}$ arises from the tenuous relationship between the measured value in the (mixed) water

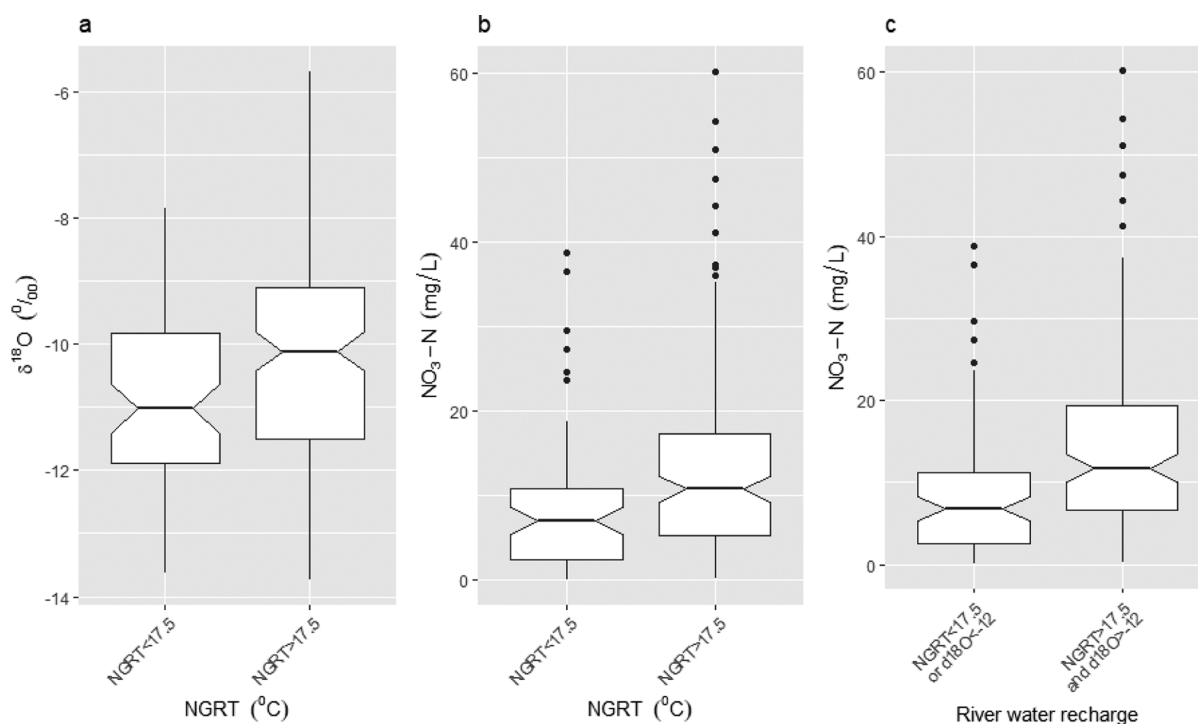


Figure 5. Boxplots showing the difference in $\delta^{18}\text{O}$ depending on NGRT (a), difference in $\text{NO}_3\text{-N}$ depending on NGRT (b), and on the combinations of the two river recharge indicators together (c). The notches indicate the 95% confidence interval of the median. The box shows the interquartile range.

sample and their distribution within an individual well water sample.^{35,73} Also, noble gas age dating does not capture variability in vadose zone travel time or processes, which may be significant.⁷⁹ Here, these are considered intrinsic to the spatio-temporal variability of nitrate loading to the water table, which is also affected by a large diversity in crops and variability in agronomic practices, soils, and climate.^{16,74}

Hydrologic Significance. Expanding the reach of previous domestic well surveys, our uniquely large geochemical survey confirms that river water as the source of recharge to groundwater and groundwater travel time are two important controlling factors of nitrate concentrations in domestic wells in the California San Joaquin Valley. Considering sample depth and $^3\text{H}/^3\text{He}$ groundwater age as proxies for groundwater travel time, an increasing trend in $\text{NO}_3\text{-N}$ is found with shorter groundwater travel times due to higher nitrogen applications over the past decades.

Recharge source and mechanism are also important controlling factors of nitrate concentrations in the domestic wells. Our findings confirm prior research on the spatial distribution of groundwater nitrate, showing that samples from domestic wells with geochemical signatures of river water recharge, either through NGRT or $\delta^{18}\text{O}$, have lower concentrations of $\text{NO}_3\text{-N}$ compared to samples that show mixed source or local precipitation recharge.⁴² Also, the wells that are further than 2 km from rivers were found to have higher $\text{NO}_3\text{-N}$ concentration than the ones that are closer than 2 km. We find that NGRT, as opposed to $\delta^{18}\text{O}$, is a better indicator of direct river water recharge. River water recharge has a curbing impact on $\text{NO}_3\text{-N}$ concentrations in domestic wells, either directly recharged or applied via irrigation, possibly far from the river.

We find that routine application of river water to augment recharge of groundwater is not expected to have a more

deteriorating effect on groundwater $\text{NO}_3\text{-N}$ concentrations than other sources of irrigation water or recharge. This has important implications in the discussion of the side effects of agricultural MAR.^{45–48}

The long travel times of nitrate documented here for the widespread nitrate contamination in an irrigated agricultural basin underscores the urgent need to address nitrate contamination both with intermediate to long-term alternative drinking water solutions^{80,81} and with plans for long-term remediation of groundwater quality through a reduction of nutrient load in agricultural fields. Because of the long travel times of groundwater, it will still take decades to achieve lower nitrate concentrations in domestic wells.^{35,40,82,83}

The most important finding in this study, that river water recharge is connected to lower nitrate concentrations, suggests that river water irrigation has a diluting effect that reduces the concentration of nitrate found in groundwater. The findings further suggest that nitrate in groundwater used for irrigation water should be carefully managed to optimize for crop nutrition. With respect to nitrate, this study confirms that agricultural MAR (“flood-MAR”) has the potential to play an important role in the remediation of groundwater quality in the SJV⁸⁴ while also replenishing aquifers in overdraft if other source water quality concerns⁸⁵ can also be addressed.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c03071>.

Surface water districts and their surface water source; map of the study area; isotopic signature of water in groundwater samples, river water recharge and local precipitation recharge; $\text{NO}_3\text{-N}$ versus well depth (five alternative well depth metrics); highest quartile $\text{NO}_3\text{-N}$

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